

PARAMETER EVALUATION FOR COPROCESSING OF BROWN COAL AND VACUUM RESIDUE FROM PETROLEUM

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INTRODUCTION

An increasing share of petroleum short - or vacuum residue (VR) from refining confronted with more heavy crudes is hard to be marketed or upgraded. Coprocessing is the attempt to coreact VR in a hydrogenative and preferable once-through operation together with an appropriate share of a suitable coal especially lignite. A report on this covering the literature till end of 1986 will be published by the European Commission (EC) in 1988 titled "coprocessing".

If the aimed for technology is once-through a limited preevaluation is possible by batch type autoclave experiments especially with respect to parameter influences. This report covers autoclave experiments for one "Rheinische" brown coal and different petroleum refining products including a light vacuum distillate (LSP); a very heavy vacuum distillate (ZYL); the vacuum residue (VR) from one single crude oil and another vacuum residue (VRW) very high in molecular weight.

EXPERIMENTAL

The coal (as reacted) is characterized by analytical data:

moisture 5.9%; ash (wf) 3.6%; volatile matter (dmf) 48.8%; xylene extract 5.8%
And the ultimate analysis (dmf): 68.3% C; 5.6% H; 1.3% S (total); 0.7% N; 24.1% O (diff)

The petroleum derived reactands (solvents) are characterized by basic analytical data:

	LSP	ZYL	VR	VRW
Conradson carbon (%)	0.04	0.27	21.7	
Asphaltenes (%)	-	-	1.6	2.1
Aromaticity (%)	16	18	50	23
Average molecular weight (VPO)	249	433	897	1410
Ultimate analysis % C	86.0	86.2	85.4	86.5
% H	11.6	11.2	9.7	11.4
% S	1.6	2.4	3.3	1.5
% N	0.1	0.1	0.4	0.4
% O (diff)	0.7	0.1	1.2	0.3

For an experiment a coal was slurried in a solvent at a ratio of 1:1.7 and 3.8% red mud and 0.6% Na₂S (referring to coal dmf) were added as catalyst. All experiments were conducted batchwise in a rocking autoclave prepressurized with hydrogen at a set initial pressure. The reactions were controlled for temperature and pressure recorded versus time. Heating and cooling rates were 0.3 K/s. After cooling back to normal temperature products gases (G) were released and analysed by TC-gaschromatography and the hydrogen uptake of the experiment was calculated from gas analysis, water produced (W) and pressure difference before and after the experiment. Non gaseous products were separated and evaluated as raw naphtha (N), medium and heavy oils (O), asphaltenes (A) (precipitated in hexane), and residue (R) (benzene insoluble) all based on feed coal (dmf). For some experiments water was not determined separately and then is contained in the figure for gases. For all solvents forgoing experiments under the same conditions provided the base of correlations for yields of products from only coal.

TEMPERATURE DEPENDENCE

For each feed combination the temperature was screened from 380 to 460°C at set conditions of 9 MPa initial hydrogen pressure and 60 min. residence time. The results are given in Table 1.

The hot system pressure decreases over the residence time for all petroleum derived solvents up to 435°C but already increases at 455°C from stronger cracking reactions in the solvent. Accordingly the hydrogen uptake does not differ or decreases from 435 to 460°C. In total the system pressure is not very much dependent

on the nature of the solvent. The hydrogen uptake in general increases with temperature and no clear dependence on the nature of the solvent exists. The conversion of coal at 380°C is independent of the nature of solvents at a constant 49 to 50%. At higher temperatures conversion is always highest in the coal derived solvent but heavy vacuum distillates from petroleum provide an almost equal conversion in the range of 410 to 435°C whereas the vacuum residue gives a low conversion independent of the temperature. Heavy solvents obviously do not prevent coking at 460°C under the conditions given. The share of asphaltene in the products in general decreases at higher temperatures but this then is dependent strongly on the nature of the solvent. In light vacuum distillate the share of coal derived asphaltene stays below 10% but in heavy distillates it is as high as 17% but then strongly reduced again at temperatures above 430°C. For the vacuum residue at 380°C almost 30% of coal derived asphaltene exist but then decrease strongly to only 2% at 460°C. It should be noticed, however, that these figures are calculated by difference and that this vacuum residue reacted alone results up to 11% asphaltene at 410°C decreased to 6% at 460°C. Reacted alone these solvents give less than 3% of asphaltene at 460°C with the already quoted exception of vacuum residue.

From experiments in petroleum derived solvents the share of product gases in the range of 10 to 13% is almost independent of the nature of solvent and on temperature. Reacted alone these solvents give 5% of gases to the most at 460°C. The higher the temperature the higher is the share of methane in all product gases. There also is a considerable content of carbon dioxide from the destruction of coal but not much influenced anymore by temperature above 380°C.

The share of naphtha in the products for petroleum derived solvents has a maximum at 410°C for vacuum distillates, increases with the boiling range of the solvent, reaches 16% for ZYL-solvent, is much lower for vacuum residue but then increasing with temperature to 11% at 460°C. The total naphtha yield combined from coal and solvent is 40% for ZYL-solvent and 33% for VR-solvent at 460°C.

The total oil yield from coal increases with the boiling range of a petroleum derived distillate solvent to a maximum at 435°C but still increasing to 460°C for the vacuum residue as a solvent. Since no true separation of product oils in shares stemming from coal or solvent is possible a characterization refers to the total product oil. In general an increase in reaction temperature decreases the atomic H/C-ratio of the product oil but still reflects the quality of each feed solvent whereas aromaticity increases with temperature rather independent of the nature of the solvent. At 435°C aromaticities of the total product oil are about 0.35 but are above 0.50 at 460°C. The average molweight of the total product oil at lower reaction temperatures are strongly dependent on the nature of the feed solvent but are equalized at 435°C for distillate solvents to an average of 250 as well as for vacuum residue but then down to 250 only at 460°C.

From recalculations and estimations for a once-through operation for the coal derived solvent the total liquid yield is 73% (M=300) at 460°C, for the vacuum residue as a solvent it is 58% (M=265) at 435°C, and for the most effective petroleum derived solvent it is 78% (M=225) at again 435°C.

RESIDENCE TIME DEPENDENCE

Since 435°C is not the temperature for a maximum gain of total products but obviously significant for the degradation of the brown coal in the mixture residence time variations in between heating-up only and 120 min. are made as presented in Tab. II). The apparent initial system pressure is dependent on the boiling range as well as on the crackability of the solvent but then much higher than from experiments with these solvents alone without addition of coal. This is due to the hydrocarbon gases and the carbondioxide produced from coal and only compensated to some degree from the hydrogen consumption.

The hydrogen uptake shortly after heating up is low and little dependent on the nature of the solvent. After 60 min. residence time it is completely independent of the nature of the solvent. The hydrogen uptake increases for 10 min. only but thereafter is obviously in equilibrium. These results are calculated by difference. For these solvents reacted without coal under the same conditions the hydrogen uptake increases four- to sixfold from 0 to 60 min. residence time and thus the data calculated for coal are limited in their evaluation.

For product gases the major component is carbondioxide produced rather spontaneously, thus explaining the small increase of gases with residence time in the range of 10 to 14%. From experiments with only solvents the share of product

gases under the same conditions stays below 2% even at 60 min. residence time. More significant are the differences in produced or retransformed asphaltenes. For short contact times they directly reflect the nature of the solvent. For the light LSP-solvent the asphaltenes derived from coal are rather independent of residence time whereas for the other distillate reach a maximum after 10 min. but then are transferred into oils by about 2% after 60 min. For vacuum residue which reacted without coal gives less than 2% asphaltenes at short contact time the coal derived asphaltenes immediately reach 33% but are transferred into oils by 25% after 30 min. From the solvents alone reacted without coal under the same conditions the product share of naphtha strongly increases with residence time reaching about 20% after 60 min. The coal derived naphtha is lower, reaches a maximum in distillate solvents after 10-30 min. but is much more dependent on the nature of the solvent. Recalculated for a once through operation this feed combination at 435°C and 30 min. residence time results to a total of 17% naphtha. For vacuum residue only 8% are gained from coal after 30 min. and a recalculated total for the feed combination would be little more than 10%. More important for the feed combinations are the yields of oil boiling above 200°C as derived from coal. In general it can be stated that the lighter the solvent the higher is the oil yield from coal. The oil yield increases almost steadily with residence time but then data are dependent on the nature of the solvent. The total liquid yield containing naphtha and heavy oils again is the higher the lighter the solvent and is in general increasing with residence time. For the light vacuum distillate as a solvent the total liquid yield from coal of 40% and of 35% for heavy vacuum distillate as a solvent are reached after 60 min. residence time. For vacuum residue as a solvent the influence of time on the total liquid yield from coal is most pronounced. From 3% occurring immediately after heating up it is increased to 26% after 30 min. residence time. Since no true separation of product oil boiling above 200°C from either coal or solvent is possible, any characterization of oil refers to the total product oil. After heating up only the H/C-ratio of the total product oil is dominated from the solvent with 1.61 for product from LSP-experiments to 1.39 for products from VR-experiments but after 60 min. it is equalized to 1.40 almost independent of the solvent. In accordance the aromaticity of the product oil almost independent of the nature of solvent increases from about 0.26 at heating up to about 0.37 after 60 min. and then is markedly higher than in the solvents themselves. The average molweight (M) of the product oil for each residence time is determined from the nature of solvent but overproportionally decreased in the experiments with the vacuum residue (initial molweight 900) with M=390 at only heating up but M=250 after 60 min. Recalculated for a once-through operation the total oil yield would be 61% with M=305 for 30 min. residence time from vacuum residue as a solvent and 74% with M=270 for 30 min. residence time from the heaviest vacuum distillate as a solvent.

PRESSURE DEPENDENCE

For comparison set conditions of 435°C and 60 min. residence time were chosen for a variation of initial hydrogen pressure of 6 to 15 MPa. This in the case of 15 MPa initial leads to unrealistic system pressures of up to 42 MPa but are tolerated here for parameter evaluation only. The experiments are limited to two petroleum derived solvents only. The results are presented in Tab. III]. The hydrogen uptake increases with initial pressure but rather independent on the nature of solvent and the gas formation is slightly reduced by pressure. For this coal in all solvents conversion increases with increasing initial pressure. For the range of 9-12 MPa initial pressure the coal conversion is the lower the heavier the nature of the solvent applied. For 15 MPa initial pressure the coal conversion might be suppressed if the hot system pressure is too high. Asphaltenes also increase with an increase of the initial pressure but for a given pressure are almost independent of the nature of the solvent. Naphtha formation is improved by a high initial pressure but not very much dependent on the nature of the solvent. For solvent (VR) the oil yield from coal scatters for initial pressures of 9-15 MPa but again is rather independent of the nature of the solvent. About 27% oil yield are gained at maximum in VR. Since no true separation of product oils from coal or solvent is possible an analytical evaluation refers to the total product oil boiling above 200°C. For coal BKR from all solvents the aromaticity of the total product oils is almost constant in a range of 0.35-0.40 against

a solvent aromaticity of about 0.2 and not systematically influenced by pressure or by the nature of the solvent. The strong destruction of coal as well as of heavy residual solvents is reflected from the average molweight (M). In LSP (M=249) the molweight of the total product oil is almost independent of the initial pressure with M=224 for 6 MPa and M=218 for 15 MPa. VR (M=897) comparable data are M=313 at 9 MPa and M=268 at 15 MPa. Based on a once-through approach recalculated total liquid yields including naphtha under the conditions given and at 12 MPa initial pressure (hot system pressure in the autoclave already above 30 MPa) and is 66% including 18% naphtha and 48% heavy product oil with M=285 in VR.

FEED MIXTURE DEPENDENCE

These experiments are based on a variation of mixtures of the same coal but a different VR-W residue described in the experimental section. The results are presented in Tab. IV) for set conditions of RMPaH, 430°C and 30 min. residence time. The system pressure is strongly influenced from the share of coal increasing by 13MPa from 0 to 67% of coal and dominated by CO₂, CO and much lesser CH₄ originating from coal. With two exceptions the pressure drops during 30 min. on temperature, however, is almost constant. Hydrogen consumption by reacting VRW is 0.48%. For coal up to about 30% the hydrogen consumption is lower than for VRW. Coal might in part provide hydrogen for radical capping of fragments from VRW. Above 30% coals' hydrogen consumption is increasing from about 0.5% to 0.67% about proportional. The coal conversion is highest at 69% for about 10% of coal, then decreasing but almost constant at about 50% for 30 to 67% of coal. Product gas formation is strongly increasing with the share of coal and is mainly CO₂ and CO. The total residue increases with the share of coal but the ratio of total residue versus coal share in the feed is about constant. A certain part of the coal does not react under the conditions given, or a part of asphaltenes are included in the residue because the total asphaltene content decreases strongly with an increasing share of coal. The naphtha formation is increasing with the share of coal but then almost constant above 30% of coal in the feed. The high boiling oils are decreasing from more coal in the feed but still above 50% for 30% of coal in the feed. The quality of these high boiling oils are improved from a higher share of coal in the feed. Only VRW or mixed with little coal results to more than 80% of total liquid yield but the quality of the product oil is insufficient with a molecular weight of or above 500. Shares of 30-40% of coal in the feed provide a total liquid yield of 70% with a molecular weight of heavy product oil at or below 400.

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Table I) Dependence on temperature
(9 MPa initial hydrogen pressure; 60 min. residence time)

Feed		Reaction parameters			
Solvent	Temperature (°C)	hot pressure beginning	(bar) end	H-up- take %	Conver- sion
1 LSP	380	243	243	0.9	48
2 LSP	410	255	247	1.1	57
3 LSP	435	265	259	1.2	62
4 LSP	460	303	346	1.2	53
5 ZYL	380	230	231	0.7	49
6 ZYL	410	240	230	1.4	63
7 ZYL	435	274	263	1.1	62
8 ZYL	460	279	332	1.1	48
9 VR	380	256	253	0.7	50
10 VR	410	276	255	1.2	50
11 VR	435	291	276	1.1	51
12 VR	460	306	335	1.3	48

continued

Product distribution (% of feed coal)						
	G	R	A	W	N	O
1	12.1	52.3	8.7	2.1	11.3	14.4
2	12.1	42.9	11.3	3.1	14.9	16.8
3	11.0	37.8	9.1	2.5	9.8	31.0
4	12.6	47.3	4.7	3.0	7.0	26.6
5	10.9	51.1	14.6	3.1	11.4	9.6
6	12.5	37.3	17.3	5.3	15.8	12.9
7	13.8	38.0	13.0	3.8	7.9	24.6
8	13.2	52.0	3.0	4.0	10.5	18.4
9	11.0	50.3	29.2	-	5.0	5.2
10	12.7	49.7	23.7	1.9	6.4	6.8
11	13.4	48.7	8.6	4.0	5.4	21.0
12	12.4	51.6	2.3	4.0	10.6	20.4

All %-results are refering to coal daf. G = gases; R = residue (benzene insoluble); A = asphaltenes (hexane insoluble); W = water; N = naphtha (boiling below 200°C); O = oil

Tab II) Dependence on residence time
(9 MPa initial hydrogen pressure; 435°C)

Feed		Reaction parameters				H-up- take %	Conver- sion %
Solvent		Residence time (min)	hot pressure begin.	end (bar)			
1	LSP	0	276			0.5	42
2	LSP	10	274	274		1.1	54
3	LSP	30	275	274		1.1	57
4	LSP	60	265	259		1.2	63
5	ZYL	0	282			0.3	44
6	ZYL	10	277	275		0.8	56
7	ZYL	30	276	265		1.1	59
8	ZYL	60	274	263		1.1	62
9	ZYL	120	275	263		1.2	59
10	VR	0	287			0.5	46
11	VR	10	289	281		0.8	49
12	VR	30	284	281		1.1	51
13	VR	60	291	276		1.1	51

continued

Product distribution (% of feed coal)						
	G	R	A	W	N	O
1	11.0	58.4	8.6	2.7	10.5	9.3
2	14.1	46.0	8.1		14.5	18.4
3	12.0	43.4	7.3	3.1	11.6	23.7
4	11.0	37.8	9.1	2.5	9.8	31.0
5	10.6	56.0	13.7	2.9	8.0	9.1
6	11.6	44.4	14.0	4.4	8.5	17.9
7	12.5	40.7	12.2	4.9	8.2	22.6
8	13.8	38.0	13.0	3.8	7.9	24.6
9	12.7	41.0	10.6	2.1	5.2	29.6
10	10.2	54.4	32.9		2.0	1.0
11	11.2	50.7	17.6	4.3	2.5	14.5
12	13.5	48.7	7.6	5.1	8.2	17.7
13	13.4	48.7	8.6	4.0	5.4	21.0

All %-results are referring to coal daf: G=gases; R=residue (benzene insoluble);
A=asphaltenes (hexane insoluble); W=water; N=naphtha (boiling below 200°C);
O=oil

Tab III) Dependence on hydrogen pressure
(435°C, 60 min residence time)

Feed		Reaction parameters			
	Solvent	initial H ₂ -pressure (bar)	hot pressure beginning	(bar) end	H-up take % Con- version %
1	LSP	60	213	251	0.8 47
2	LSP	90	265	259	1.2 62
3	LSP	120	327	315	1.8 63
4	LSP	150	408	375	1.8 66
5	VR	90	291	276	1.1 51
6	VR	120	361	319	1.5 61
7	VR	150	420	371	1.8 64

continued

Product distribution (% of feed coal)						
	G	R	A	W	N	O
1	14.9	52.6	4.2	4.4	8.4	16.3
2	11.0	37.8	9.1	2.5	9.8	31.0
3	14.1	36.9	7.9	3.5	10.0	29.4
4	13.8	33.9	8.7	3.6	10.4	31.4
5	13.4	48.7	8.6	3.1	6.3	21.0
6	11.4	39.1	9.3	3.6	11.2	26.9
7	11.4	36.1	9.0	5.4	14.8	25.1

All %-results are referring to coal daf: G=gases; R=residue (benzene insoluble);
A=asphaltenes (hexane insoluble); W=water; N=naphtha (boiling below 200°C);
O=oil

Tab IV) Dependence on feed mixture
mixtures of coal and residue VRW without catalyst addition
(conditions 430°C; 12 MPa initial hydrogen pressure; 30 min.
residence time)

Feed %			Reaction parameters			
No	VRW	coal dmf	hot pressure (bar)		H-up- take % (of coal)	Conver- sion of coal %
			beginning	end		
1	100	0	301	289	0.48	-
2	91	9	312	299	0.35	69
3	83	17	330	317	0.46	55
4	71.5	28.5	360	340	0.56	53
5	61.5	38.5	372	359	0.59	50
6	50	50	389	373	0.64	47
7	33	67	430	392	0.67	50

Product distribution (% of feed)

	G	R	A	W	N	O	M (average mol weight of total heavy oil)
1	0.5	4.5	9.3	-	12.1	74.1	471
2	2.4	3.8	6.9	-	11.3	76.0	520
3	2.6	11.8	7.3	0.9	13.0	64.9	448
4	3.2	17.7	5.8	0.9	21.3	51.7	409
5	4.3	20.7	5.9	2.5	19.2	48.0	373
6	6.3	26.9	2.5	6.7	19.0	39.2	363
7	9.0	33.1	2.1	8.3	19.4	28.7	360

All %-results are referring to total feed (dmf): G=gases; R=residue (benzene insoluble); A=asphaltenes (hexane insoluble); W=water; N=naphtha (boiling below 200°C); O=oil